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Le commissaire aux brevets a reçu une demande de délivrance de brevet visant une invention. Ladite requête satisfait aux exigences de la *Loi sur les brevets*. Le titre et la description de l'invention figurent dans le mémoire descriptif, dont une copie fait partie intégrante du présent document.

Le présent brevet confère à son titulaire et à ses représentants légaux, pour une période expirant vingt ans à compter de la date du dépôt de la demande au Canada, le droit, la faculté et le privilège exclusif de fabriquer, construire, exploiter et vendre à d'autres, pour qu'ils l'exploitent, l'objet de l'invention, sauf jugement en l'espèce rendu par un tribunal compétent, et sous réserve du paiement des taxes périodiques.

The Commissioner of Patents has received a petition for the grant of a patent for an invention. The requirements of the *Patent Act* have been complied with. The title and a description of the invention are contained in the specification, a copy of which forms an integral part of this document.

The present patent grants to its owner and to the legal representatives of its owner, for a term which expires twenty years from the filing date of the application in Canada, the exclusive right, privilege and liberty of making, constructing and using the invention and selling it to others to be used, subject to adjudication before any court of competent jurisdiction, and subject to the payment of maintenance fees.

BREVET CANADIEN **2,262,925** CANADIAN PATENT

Date à laquelle le brevet a été accordé et délivré	2002/03/26	Date on which the patent was granted and issued
Date du dépôt de la demande	1997/07/30	Filing date of the application
Date à laquelle la demande est devenue accessible au public pour consultation	1998/02/12	Date on which the application was made available for public inspection

Commissaire aux brevets / Commissioner of Patents

Canada

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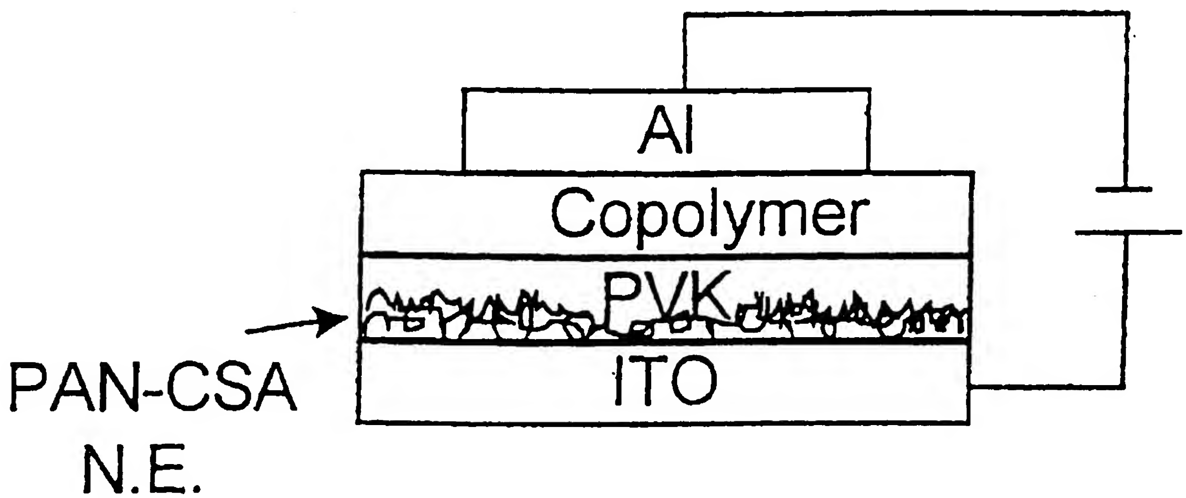
(54) Titre : DISPOSITIFS ELECTROLUMINESCENTS UTILISANT DES ELECTRODES DE TRAVAIL D'EXTRACTION
(54) Title: LIGHT-EMITTING DEVICES UTILIZING HIGH WORKFUNCTION ELECTRODES



(57) Abrégé/Abstract:
The present invention includes light emitting device incorporating light emitting polymeric material. The device contains a transparent cathode having conducting material with a first work function value, an electron transporting polymer or hole transporting polymer having an electron affinity value and ionization value, and an anode having conducting material with a second work function value.

LIGHT-EMITTING DEVICES UTILIZING HIGH WORKFUNCTION ELECTRODES

Technical Field

The present invention is in the field of light-emitting polymers and light emitting devices produced therefrom.

Background

Since the report in 1990 of electroluminescence (EL) in poly(*p*-phenylene vinylene) (PPV) [1], EL of conjugated polymers has been considered an important property with many potential applications. Electroluminescence combined with other unique properties of polymers, such as solution processibility, band gap tunability, and mechanical flexibility, make conjugated polymers excellent candidates for low cost large area display applications. In addition to PPV, a variety of PPV derivatives and other conjugated polymers and copolymers have been found to exhibit electroluminescent properties [2,3]. Light-emitting devices incorporating these materials have demonstrated all the necessary colors needed for display applications.

Since the initial fabrication, a number of techniques have been developed to improve the device performance. One way is to use a low workfunction metal, such as Ca, as the electron injecting electrode (cathode) [4]. The double charge injection mechanism of polymer light-emitting diodes (LEDs) requires the match of cathode (anode) workfunction to the corresponding LUMO (HOMO) level of the polymer in order to achieve efficient charge injection. The relatively small electron affinity of most conjugated polymers requires metals with very low workfunctions to achieve efficient electron injection. However, since low

The anode material may be any metal having sufficiently high workfunction such as will facilitate electron flow through the light emitting device, which flow is inverted as compared to prior art devices. Such metals may be such metals as gold metal and similar metals and alloys.

The substantially transparent cathode material may be material that facilitates electron flow through the light emitting device, such as indium-tin-oxide metal. wherein said substantially transparent cathode comprises indium-tin-oxide metal. The substantially transparent cathode material also may comprise a conducting polyanilines, including camphor sulfonic acid doped polyanilines, and conducting polypyrroles.

These devices may be constructed in accordance with deposition and assembly techniques known in the art. The present invention may be used in the creation of a wide variety of lighting and lighted displays, giving the many advantages associated with polymeric materials.

In accordance with the present invention, the preferred embodiment is a light-emitting device based on the pyridine-containing polymers and copolymers in various device configurations. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al or even ITO as electron injecting contacts. Taking advantages of the better electron transport properties of the pyridine-containing polymers, we fabricate bilayer devices utilizing poly(9-vinyl carbazole) (PVK) as hole transporting/electron blocking polymer, which improves the device efficiency and brightness significantly due to the charge confinement and exciplex emission at the PVK/emitting polymer interface. The incorporation of conducting polyaniline network electrode to PVK reduces the device turn on voltage significantly while maintaining the high efficiency. The control of the aggregation in the polymer films by blending with insulating host polymers open up the possibility of

making voltage-controlled multi-color light-emitting devices. The capability of eliminating the use of low workfunction metals makes the pyridine based polymers an excellent candidate for polymer light-emitting devices.

Brief Descriptions of the Drawings

Figure 1 shows the chemical structures of pyridine-based conjugated polymers and copolymers: (a) poly(p-pyridine) (PPy), (b) poly(p-pyridyl vinylene) (PPyV), (c) copolymers of PPyV and PPV derivatives (PPyVP(R)$_2$V) with various functional sidegroups R = $C_{12}H_{25}$, $OC_{16}H_{33}$, $COOC_{12}H_{25}$, and (d) strapped copolymer (@PPyVPV).

Figure 2 shows a schematic structure of a bilayer device with conducting polyaniline network electrode in accordance with one embodiment of the present invention.

Figure 3 shows a normalized optical absorption (dashed line) and PL of the strapped copolymer film (solid line), EL of a single layer device (solid line with dots), and PL of solution in xylenes (dotted line).

Figure 4 shows a comparison of (a) light-voltage and (b) light-current characteristics for a single layer device (square), a bilayer device (circle), and a bilayer device with PAN-CSA network (triangle). Inset: EL spectra for the single layer device (dashed line), the bilayer device (solid line), and the bilayer device with network electrode (dotted line).

Figure 5 shows a film PL of the pure wrapped copolymer and its blends with PMMA in various ratios with an excitation energy of 2.65 eV, and solution PL of the copolymer in xylenes. Inset: Film PL of a 1:20 blend with different excitation energies as indicated in the graph. Spectra are offset for clarity.

Figure 6 shows a schematic structure of an inverted light-emitting devices with PPy as emitting layer and PVK as hole transporting layer.

Detailed Description of the Preferred Embodiments

In accordance with the foregoing summary of the invention, the following presents a detailed description of the preferred embodiment of the invention which is presently considered to be its best mode.

The synthesis of the pyridine-containing polymers has been reported earlier [9-10]. For single layer devices, the emitting layer was spin-cast from solutions in formic acid (for PPy and PPyV) or xylenes (for copolymers) (with a concentration ~10 mg/ml) onto pre-cleaned patterned ITO substrates with sheet resistance of ~15 Ω/square at 1000-2000 rpm. For bilayer devices, PVK layer was spin coated onto ITO substrate from solution in tetrahydrofuran (THF) (~10 mg/ml) at ~3000 rpm. The emitting layer was then spin coated on top of the PVK layer from appropriate solutions. The conducting polyaniline network electrode was formed by a spin-cast blend of camphor sulfonic acid doped polyaniline (PAN-CSA) and low molecular weight host polymer poly(methyl methacrylate) (PMMA) (from Aldrich Chemical Co.) in an appropriate ratio in *m*-cresol. The host polymer PMMA was subsequently washed away by xylenes. The PVK and emitting layers were similarly coated as in the bilayer device. All solutions were filtered using Gelman Acrodisc CR PTFE 1μm filters. The top metal electrode was deposited by vacuum evaporation at a pressure below 10^{-6} torr. To prevent damage to the polymers, the substrate was mounted on a cold-water cooled surface during evaporation. Figure 2 shows schematically the structure of a bilayer device with PAN-CSA network electrode.

Absorption spectra were measured on spin-cast films using a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrometer. Photoluminescence (PL) and EL were measured using a PTI fluorometer (model QM-1). The current-voltage (I-V) characteristics were measured

simultaneously with EL using two Keithley 195A multimeters while dc voltage was applied by a HP 6218A DC power supply.

Figure 3 shows the optical absorption and PL of the strapped copolymer film and EL of a single layer device. For comparison, the PL of the strapped copolymer solution in xylenes is also shown. The film PL peaks at 2.05 eV with a shoulder at 2.25 eV. As compared to the film absorbance, the peak of the film PL is redshifted 0.55 eV, which is attributed to the aggregates formed in the film [12]. The shoulder is suggested to come from the unaggregated site, and is supported by the PL measurements of blends in PMMA (see below). It is noted that although the strapped and the corresponding unstrapped copolymer show similar features in solution PL, no shoulder is found in the film PL for the unstrapped copolymer, indicating that the strapped side chains partially break the aggregates formation in the film. The reversed oscillator strength of the EL as compared to PL suggesting that the EL come mainly from unaggregated sites, although there is also a significant contribution from the aggregate emission.

Figure 4 compares the light-voltage (L-V) and EL-current (EL-I) characteristics for a single layer device, a bilayer device, and a bilayer device with PAN-CSA network electrode using the strapped copolymer as emitting layer. As compared to those of the single layer device, the quantum efficiency and brightness of the bilayer device increase more than two orders of magnitude, reaching ~0.3% and ~300 cd/m^2 respectively. PVK is a well known hole transporting/electron blocking polymer. Besides the function of enhance the transport of holes injected from anode, it blocks the transport of electrons injected from cathode such that the electrons accumulate at the PVK/copolymer interface. This greatly enhance the probability of radiative recombination. In addition, the PVK layer separates the recombination zone from the

Conclusion

In summary, pyridine containing conjugated polymers and copolymers are excellent candidates for polymer light-emitting devices. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al or even ITO as efficient electron injecting contacts. Taking advantages of the better electron transport properties of the pyridine-containing polymers, we fabricate bilayer devices utilizing PVK as hole transporting/electron blocking polymer. The bilayer device structure improves the device quantum efficiency and brightness significantly due to the charge confinement and the exciplex emission at the PVK/emitting polymer interface. The incorporation of the conducting polyaniline network electrode to PVK reduces the device turn on voltage significantly while maintaining the high efficiency and brightness of the bilayer device. The control of the aggregation in the polymer films by blending with insulating host polymers opens up the possibility of making voltage-controlled multi-color light-emitting devices.

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In view of the present disclosure or through practice of the present invention, it will be within the ability of one of ordinary skill to make modifications to the present invention, such as through the use of equivalent arrangements and compositions, in order to practice the invention without departing from the spirit of the invention as reflected in the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A light emitting device, said device comprising:

(a) a substantially transparent cathode comprising a conducting material having a first work function value; said cathode in contact with

(b) an electron transporting/hole transporting polymer having an electron affinity value and ionization value; said electron transporting/hole transporting polymer in contact with

(c) an anode comprising a conducting material having a second work function value;

(d) a source of electrical current so as to supply said cathode with a flow of electrons; and said first work function value and said electron affinity being such as to allow said flow of electrons to flow into said electron transporting/hole transporting polymer, and said second work function value and said ionization value being such as to allow a flow of holes from said anode to said electron transporting/hole transporting polymer, so as to cause an electroluminescent emission from said device.

2. A light emitting device according to claim 1, wherein said electron transporting/hole transporting polymer comprises a pyridine-containing conjugated polymer.

3. A light emitting device according to claim 1, wherein said anode comprises gold metal.

4. A light emitting device according to claim 1, wherein said cathode comprises indium-tin-oxide metal.

5. A light emitting device according to claim 1, wherein said substantially transparent cathode comprises conducting polyaniline.

6. A light emitting device according to claim 1, wherein said substantially transparent cathode comprises camphor sulfonic acid doped polyaniline.

7. A light emitting device according to claim 1, wherein said substantially transparent cathode comprises conducting polypyrrole.

8. A light emitting device, said device comprising:

(a) an substantially transparent cathode comprising a conducting material having a first work function value; said cathode in contact with

(b) an electron transporting polymer having a electron affinity; said electron transporting polymer in contact with

(c) a hole transporting polymer having an ionization value; said hole transporting polymer in contact with

(d) an anode comprising a conducting material having a second work function value; and

(e) a source of electrical current so as to supply said cathode with a flow of electrons;

said first work function value and said electron affinity being such as to allow said flow of electrons to flow into said electron transporting polymer, and said second work function value and said ionization value being such as to allow flow of a holes from said anode to said hole transporting polymer, so as to cause an electroluminescent emission from said device.

9. A light emitting device according to claim 8, wherein said electron transporting polymer comprises a pyridine-containing conjugated polymer.

10. A light emitting device according to claim 8, wherein said hole transporting polymer is selected from the group consisting of poly(vinylcarbazole).

11. A light emitting device according to claim 8, wherein said anode comprises gold metal.

12. A light emitting device according to claim 8, wherein said substantially transparent cathode comprises indium-tin-oxide metal.

13. A light emitting device according to claim 8, wherein said substantially transparent cathode comprises conducting polyaniline.

14. A light emitting device according to claim 8, wherein said substantially transparent cathode comprises camphor sulfonic acid doped polyaniline.

15. A light emitting device according to claim 8, wherein said substantially transparent cathode comprises conducting polypyrrole.

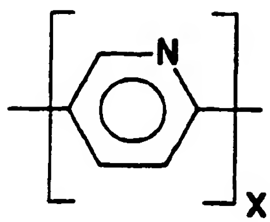


Fig. 1A

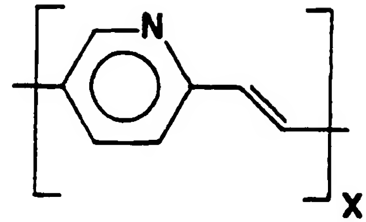
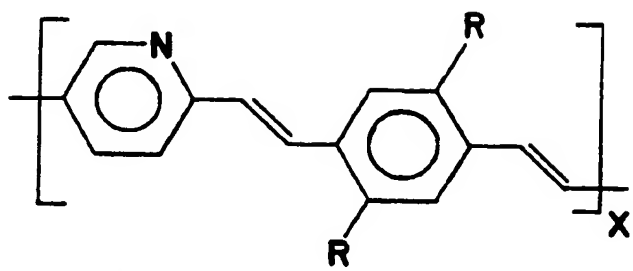
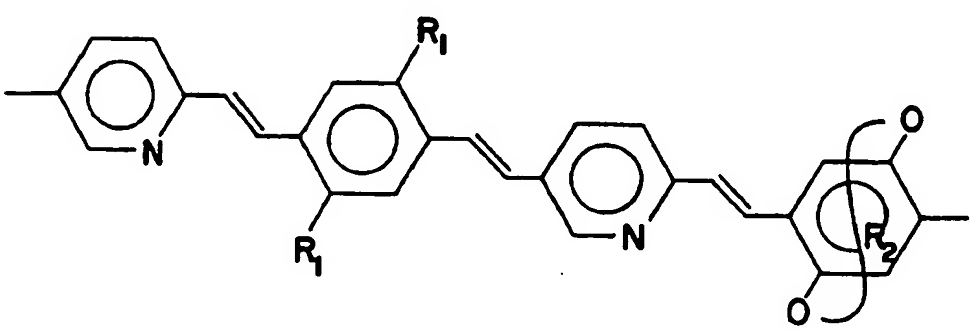


Fig. 1B



R = $C_{12}H_{25}$, $COOC_{12}H_{25}$, $OC_{16}H_{33}$

Fig. 1C



R =$OC_{16}H_{33}$, R = $(CH_2)_{10}$

Fig. 1D

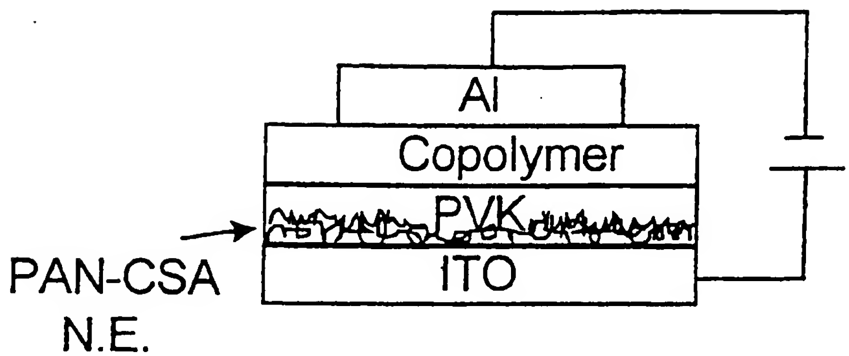


Figure 2

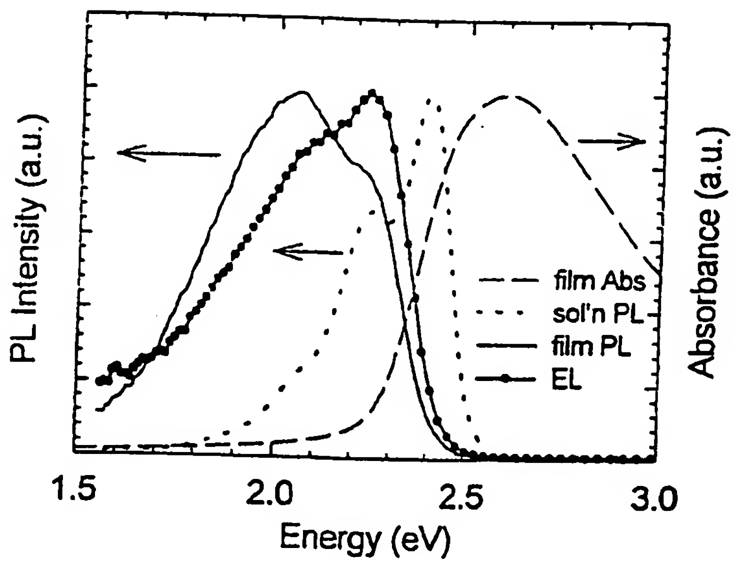

PL Intensity (a.u.)
Absorbance (a.u.)
film Abs
sol'n PL
film PL
EL
1.5
2.0
2.5
3.0
Energy (eV)

Figure 3

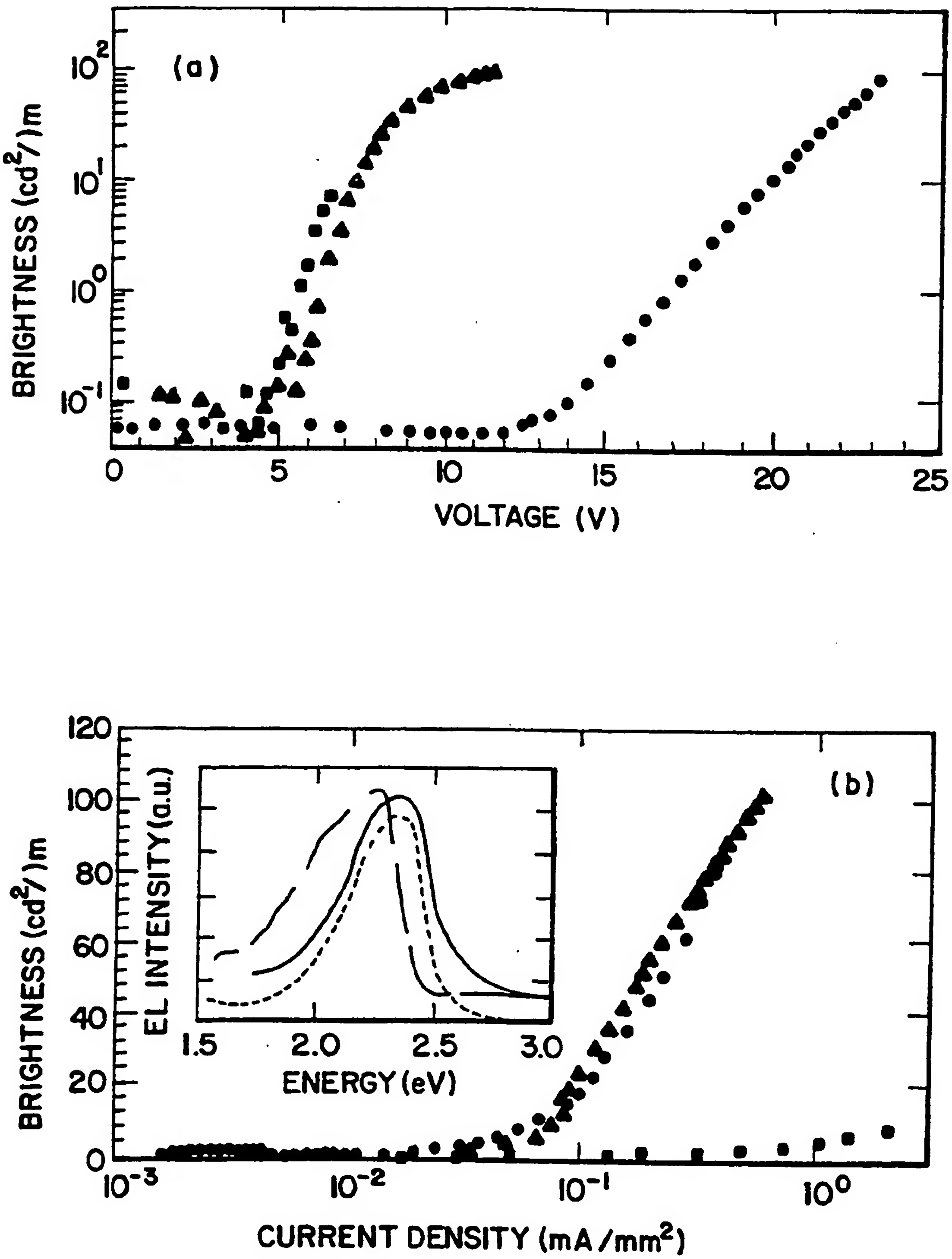


Fig. 4

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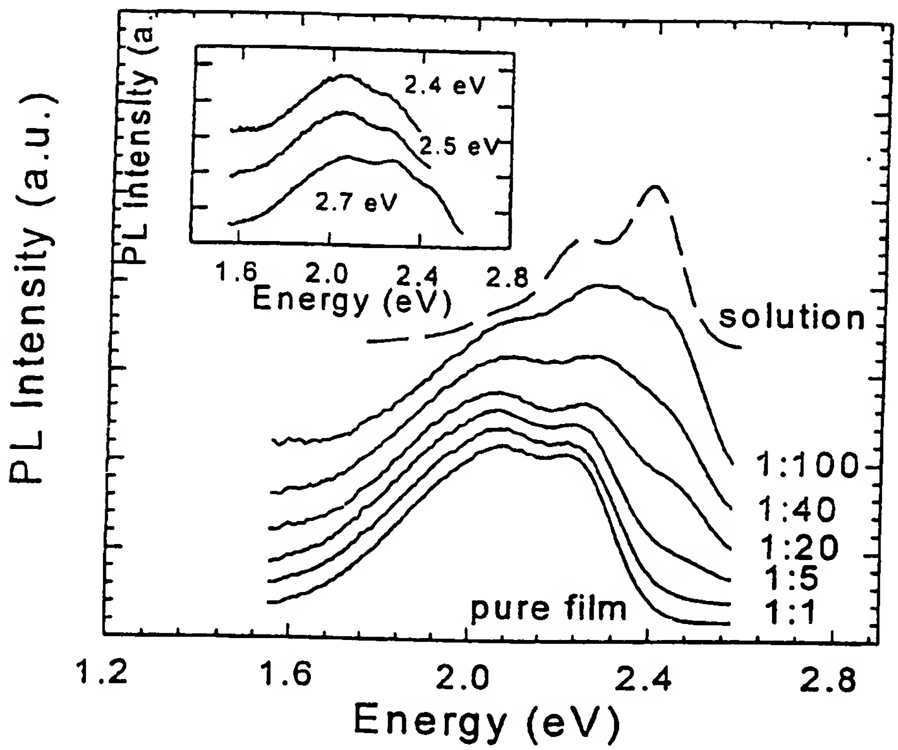
PL Intensity (a.u.)
PL Intensity (a
2.4 eV
2.5 eV
2.7 eV
1.6
2.0
2.4
2.8
Energy (eV)
solution
1:100
1:40
1:20
1:5
1:1
pure film
1.2
1.6
2.0
2.4
2.8
Energy (eV)

Figure 5

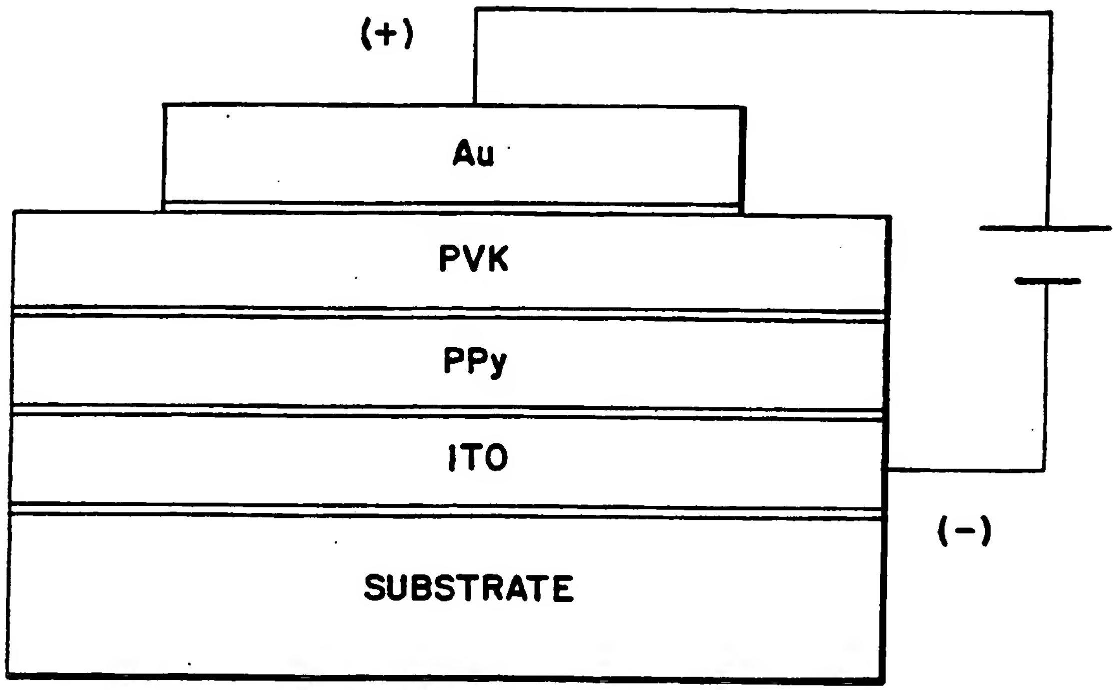

Fig. 6